Tetrahedron 67 (2011) 6917–6926

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis, structure and photo-physical properties of phosphorus-supported fluorescent probes

Vadapalli Chandrasekhar *, Mrituanjay D. Pandey, Biswanath Das, Bani Mahanti, Kandasamy Gopal, Ramachandran Azhakar

Department of Chemistry, Indian Institute of Technology—Kanpur, Kanpur 208016, India

ARTICLE INFO

Article history:
Received 27 May 2011
Received in revised form 16 June 2011
Accepted 23 June 2011
Available online 28 June 2011

Keywords:
Phosphorus-supported ligands
Hydrazides
Hydrazones
Fluorescence

ABSTRACT

Various phosphorus-supported fluorescent probes have been synthesized by the condensation reaction of multi-functional phosphorus hydrazides with various fluorophore-containing carboxaldehydes. Compounds, thus prepared, in this study are $(PhO)_2P(O)[N(Me)-N=CH-R]$ (**1a**, **1b**), $Ph_2P(O)[N(Me)-N=CH-R]$ (**2b**, **2c**, **2d**), $PhP(O)[N(Me)-N=CH-R]_2$ (**3b**, **3c**), $P(S)[N(Me)-N=CH-R]_3$ (**4b**, **4c**), $P(O)[N(Me)-N=CH-R]_3$ (**5a**, **5b**, **5c**), $N_3P_3(O_2C_{12}H_8)_2[N(Me)-N=CH-R]_2$ (**6a**, **6b**, **6c**), $N_3P_3(O_2C_{12}H_8)[N(Me)-N=CH-R]_4$ (**7a**, **7b**, **7c**, **7d**) and $N_3P_3[N(Me)-N=CH-R]_6$ (**8b**, **8c**), where R=1-*pyrenyl* (**a**), 9-*anthracenyl* (**b**), 9-*phenanthryl* (**c**) and 7-(*N*,*N*′-diethylamino)-3-*coumarinyl* (**d**). All of these compounds have been characterized by various analytical techniques including $^{31}P\{^1H\}$ NMR spectroscopy. Compounds **1b**, **2b**, **3b**, **4b**, **5b**, **5c** and **6d** have also been characterized by single crystal X-ray analysis. All of these phosphorus-supported compounds exhibit excellent fluorescence properties in aqueous solution at near physiological conditions.

1. Introduction

In recent years there have been efforts to utilize functional inorganic rings and cages as scaffolds for assembling molecules that possess dendrimer-like architectures. Thus, compounds, such as cyclophosphazenes,[1] cyclosiloxanes,[2] borazines[3] and Al–N/C rings[4] have been examined for this purpose. In all these cases the central 'inorganic core', which contains several reactive sites, are utilized for introducing the required functional groups on the periphery of the molecule. In this regard, we have been interested for some time in the use of phosphorus hydrazides for the construction of multi-site coordination ligands and for preparing electroactive dendrimer-like compounds. Thus, we have shown that the reaction of $N_3P_3[N(Me)-NH_2]_6$ with ferrocene carboxaldehyde affords the hexaferrocene starburst-type compound $N_3P_3[N(Me)-N=CH-Fc]_6$.[5] Such hydrazides and related compounds have earlier also been used, in pioneering studies, by Majoral and co-workers for the construction of macrocycles, cryptands and dendrimers.[6] The simple coordination properties of these compounds were examined by Katti and co-workers.[7] We have been interested in elaborating the chemistry of cyclic and acyclic phosphorus(V) hydrazides for a variety of reasons including assembling multifunctional ligands. Such ligands have been used to build mono- or trimetallic complexes while some others have been used to prepare heteronuclear trimetallic **3d**–**4f** complexes.[8] Some members of the former family show NLO properties while some members of the latter family possess interesting magnetic properties including single-molecule magnetism (SMM) behaviour. Though a large number of phosphorus(V) hydrazone based ligands have been studied over the years, their utility to assemble multichromophoric constructs have remained unexplored. Accordingly, in this paper, we describe the modular design, assembly and structural characterization of a family of phosphorus-supported hydrazones containing a variety of chromophores: $(PhO)_2P(O)[N(Me)-N=CH-R]$ (**1a**, **1b**), $Ph_2P(O)[N(Me)-N=CH-R]$ (**2b**, **2c**, **2d**), $PhP(O)[N(Me)-N=CH-R]_2$ (**3b**, **3c**), $P(S)[N(Me)-N=CH-R]_3$ (**4b**, **4c**), $P(O)[N(Me)-N=CH-R]_3$ (**5a**, **5b**, **5c**), $N_3P_3(O_2C_{12}H_8)_2[N(Me)-N=CH-R]_2$ (**6a**, **6b**, **6c**), $N_3P_3(O_2C_{12}H_8)[N(Me)-N=CH-R]_4$ (**7a**, **7b**, **7c**, **7d**) and $N_3P_3[N(Me)-N=CH-R]_6$ (**8b**, **8c**) where R=1-pyrenyl (**a**), 9-anthracenyl (**b**), 9-phenanthrenyl (**c**) and 7-(*N*,*N*′-diethylamino)-3-coumarinyl (**d**). The variation of the fluorescent group on the periphery of the phosphorus-supported construct from one to six in a well-planned modular manner results in interesting fluorescence behaviour.

2. Results and discussion

2.1. Synthesis and structure

A series of fluorophore-containing acyclic phosphorous hydrazones, **1a**–**b**, **2a**–**d** (monohydrazones); **3a**–**d** (dihydrazones) and

* Corresponding author. Tel.: +91 512 259 7259; fax: +91 512 259 7436; e-mail address: vc@iitk.ac.in (V. Chandrasekhar).

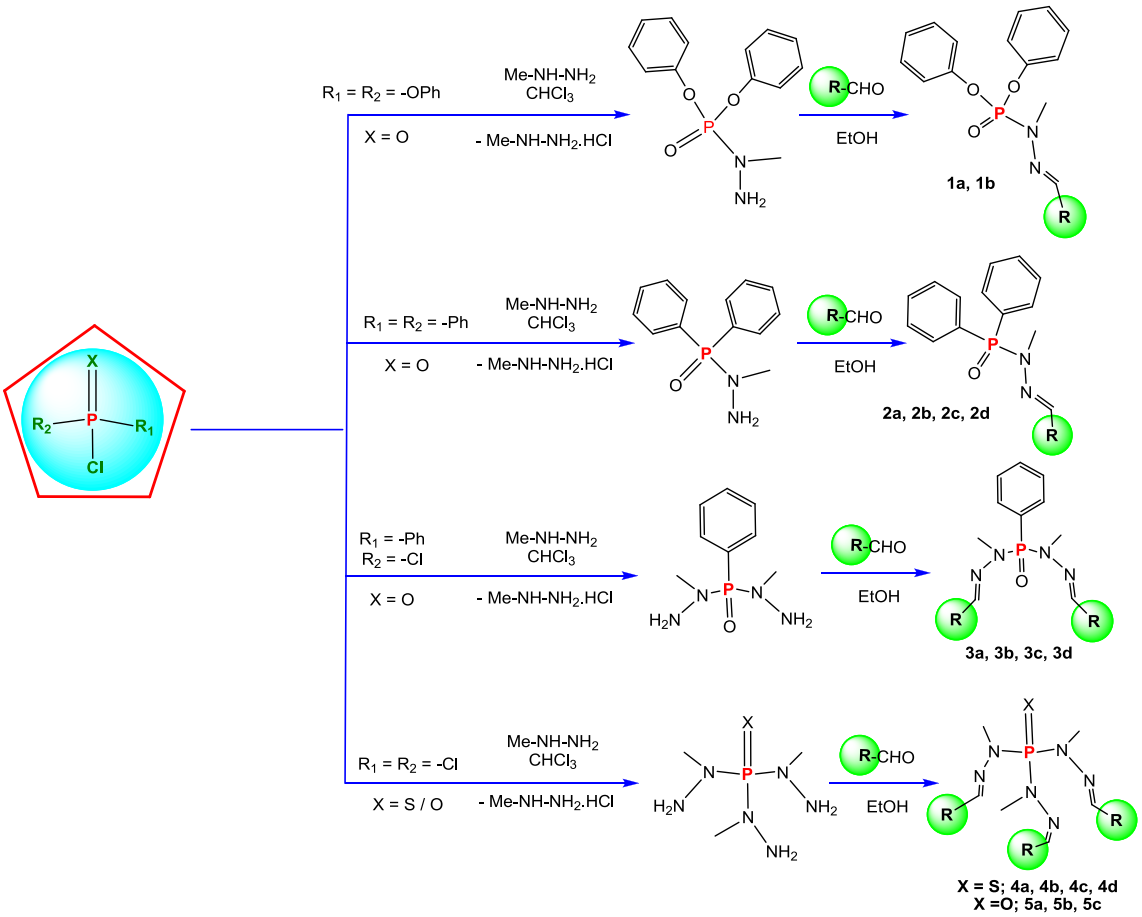
0040-4020/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2011.06.073

4a–**d**, **5a**–**c** (trihydrazones) have been synthesized by a two-step synthetic protocol. The first step involved the regiospecific reaction of *N*-methylhydrazine with an appropriate phosphorus halide [$Ph_2P(O)Cl$, $(PhO)_2P(O)Cl$, $PhP(O)Cl_2$ and $P(O)Cl_3$] affording the corresponding hydrazides: $Ph_2P(O)[N(Me)NH_2]$, $(PhO)_2P(O)[N(Me)NH_2]$, $PhP(O)[N(Me)NH_2]_2$ and $P(O)[N(Me)NH_2]_3$ (Scheme 1). Each of these functional hydrazides are endowed with reactive $-NH_2$ groups. Utilizing the reactivity of the latter condensation of the hydrazides with a fluorophore-containing carboxaldehyde [pyrene-1-carboxaldehyde (**a**), anthracene-9-carboxaldehyde (**b**), phenanthrene-9-carboxaldehyde (**c**) and 7-(*N*,*N*′-diethylamino)-coumarin-3-aldehyde (**d**)] afforded phosphorus-supported hydrazones, which contained the fluorophores as pendant groups, in near quantitative yields (Scheme 1). Utilizing a similar procedure, except replacing the acyclic phosphorus halides with chlorocyclophosphazenes ($N_3P_3Cl_2(O_2C_{12}H_8)_2$, $N_3P_3Cl_4(O_2C_{12}H_8)$ and $N_3P_3Cl_6$) resulted in the assembly of the formation of the multichromophoric cyclotriphosphazene constructs: **6a**–**d** (dihydrazones), **7a**–**d** (tetrahydrazones) and **8a**–**d** (hexahydrazones) (Scheme 2). All of these phosphorus-supported hydrazides and hydrazones are very lipophilic and are soluble in a wide range of organic solvents. The synthetic details and characterization data of some of these compounds viz., **2a**, **3a**, **3d**, **4a**, **4d**, **6d**, **8a** and **8d** have been described by us earlier.[9] All the other compounds have been well characterized by $^{31}P\{^1H\}$ NMR spectroscopy (Table 1). In addition, these compounds have also been characterized by various spectroscopic methods viz. IR, ^1H NMR and ESI–HRMS (see Experimental section). Compounds **1b**, **2b**, **3b**, **4b**, **5b**, **5c** and **6d** have also been characterized by single crystal X-ray analysis.

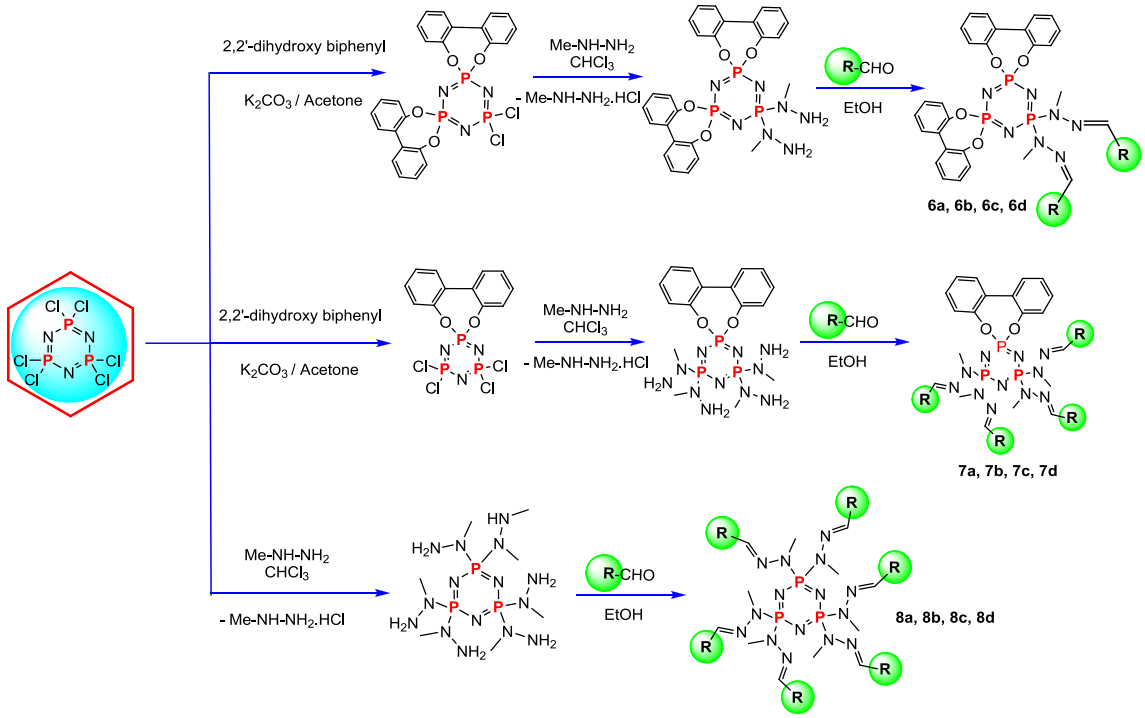
The molecular structures of compounds **1b**, **2b**, **3b**, **4b**, **5b**, **5c** and **6d** are shown in Fig. 1a–g and their selected bond parameters are given in Table 2.

Compound **1b** crystallizes in the orthorhombic crystal system (space group: $P2_12_12_1$), **2b** in the monoclinic crystal system (space group: $P2_1/n$) while **3b**, **4b**, **5b** and **6d** crystallize in the triclinic crystal system (space group: $P\bar{1}$). Compound **5c** crystallizes in the monoclinic crystal system (space group: $C2/c$). The molecular structure of the acyclic phosphorous hydrazones compounds are fairly similar and show a distorted tetrahedral phosphorus atom that acts as a pivot to anchor the chromophoric pendant groups (Fig. 1). The P=O bond distances observed in **1b** (1.452 (2) Å), **2b** (1.477 (2) Å), **3b** (1.474 (2) Å), **5b** (1.443 (3) Å) and **5c** (1.455 (5) Å) are very close to each other and are comparable with the literature values (Table 2).[10] Similarly, the P=S bond distance in **4b** is 1.925 (2) Å, which is also comparable with the literature values.[10] The P–N bond distances in **1b**–**5b** and **5c** are 1.651 (3), 1.677 (2), 1.686 (2), 1.674 (2), 1.654 (4) and 1.678 (6) Å, respectively, which are comparable with the P–N single bond distance of ~1.70 Å found in the literature (Table 2).[11]

The molecular structure of **6d** shows two 2,2′-biphenoxy units that are attached to P1 and P2 in a spirocyclic manner and are perpendicular to the plane of the cyclophosphazene core (Fig. 1g). The other phosphorous atom, P3 contains the two hydrazone units (N4 and N7). The average P–N bond distance of 1.58 Å observed for the cyclophosphahzene ring (P_3N_3 ring) is smaller than the exocyclic average P–N bond distances of 1.68 Å. In general, the P–N bond distances within the P_3N_3 ring are non-equivalent for compounds of the type *gem*-$N_3P_3X_2Y_4$.[12] Accordingly in the present



Scheme 1. Synthesis of compounds **1**–**5**. R=1-pyrenyl (a); 9-anthracenyl (b); 9-phenanthryl (c) and 7-(*N*,*N*′-diethylamino)-3-coumarinyl (d).



Scheme 2. Synthesis of compounds **6**–**8**. R=1-pyrenyl (a); 9-anthracenyl (b); 9-phenanthryl (c) and 7-(*N*,*N*′-diethylamino)-3-coumarinyl (d).

Table 1
Summary of the $^{31}P\{^{1}H\}$ NMR spectra of various precursors and hydrazone products

S.No	*P*-Halide	*P*-Hydrazide	*P*-Hydrazone
1	$(PhO)_2P(O)Cl$ −4.7 (s)	$(PhO)_2P(O)[N(Me)–NH_2]$ 0.30 (s, 1P, PO)	$(PhO)_2P(O)[N(Me)–N=CH–R]$ (**1a**): −5.01 (s) $(PhO)_2P(O)[N(Me)–N=CH–R]$ (**1b**): −5.06 (s)
2	$Ph_2P(O)Cl$ 44.9 (s)	$Ph_2P(O)[N(Me)–NH_2]$ 32.75 (s, 1P, PO)	$Ph_2P(O)[N(Me)–N=CH–R]$ (**2b**); 32.76 (s) $Ph_2P(O)[N(Me)–N=CH–R]$ (**2c**): 30.82 (s) $Ph_2P(O)[N(Me)–N=CH–R]$ (**2d**): 32.38 (s)
3	$PhP(O)Cl_2$ 39.7 (s)	$PhP(O)[N(Me)–NH_2]_2$ 29.9 (s, 1P, PO)	$PhP(O)[N(Me)–N=CH–R]_2$ (**3b**): 25.54 (s) $PhP(O)[N(Me)–N=CH–R]_2$ (**3c**): 27.19 (s)
4	$P(S)Cl_3$ 31.7 (s)	$P(S)[N(Me)–NH_2]_3$ 84.5 (s, 1P, PS)	$P(S)[N(Me)–N=CH–R]_3$ (**4b**): 74.64 (s) $P(S)[N(Me)–N=CH–R]_3$ (**4c**): 75.20 (s)
5	$P(O)Cl_3$ −2.1 (s)	$P(O)[N(Me)–NH_2]_3$ 26.0 (s, 1P, PO)	$P(O)[N(Me)–N=CH–R]_3$ (**5a**): 16.36 (s) $P(O)[N(Me)–N=CH–R]_3$ (**5b**): 16.45 (s) $P(O)[N(Me)–N=CH–R]_3$ (**5c**): 16.85 (s)
6	$N_3P_3Cl_6$ 19.5 (s)	$N_3P_3(O_2C_{12}H_8)_2$ $[N(Me)–NH_2]_2$ 26.6 (d, 2P, $P(O_2C_{12}H_8)_2$), 29.3 (t, 1P, *P*(N(Me)–NH_2), ^3J(P–N–P)=58.2 Hz.	$N_3P_3(O_2C_{12}H_8)_2[N(Me)–N=CH–R]_2$ (**6a**): 19.8 (t, 1P, *P*(N(Me)–N=CH–R), 26.6 (d, 2P, $P(O_2C_{12}H_8)$) ^3J(P–N–P)=70.9 Hz.
	$N_3P_3Cl_2(O_2C_{12}H_8)_2$ 19.8 (d, 2P, $P(O_2C_{12}H_8)$), 29.2 (t, 1P, PCl_2) ^3J(P–N–P)=80 Hz.		$N_3P_3(O_2C_{12}H_8)_2[N(Me)–N=CH–R]_2$ (**6b**): 19.0 (t, 1P, *P*(N(Me)–N=CH–R), 26.4 (d, 2P, $P(O_2C_{12}H_8)$) ^3J(P–N–P)=70.9 Hz. $N_3P_3(O_2C_{12}H_8)_2[N(Me)–N=CH–R]_2$ (**6c**): 19.8 (t, 1P, *P*(N(Me)–N=CH–R), 26.6 (d, 2P, $P(O_2C_{12}H_8)$) ^3J(P–N–P)=70.9 Hz.
7	$N_3P_3Cl_6$ 19.5 (s)	$N_3P_3(O_2C_{12}H_8)$ $[N(Me)–NH_2]_4$ 27.2 (t, 1P, $P(O_2C_{12}H_8)$), 29.9 (d, 2P, *P*(N(Me)–NH_2), ^3J(P–N–P)=53.4 Hz.	$N_3P_3(O_2C_{12}H_8)[N(Me)–N=CH–R]_4$ (**7a**): 19.9 (d, 2P, *P*(N(Me)–N=CH–R), 26.8 (t, 1P, $P(O_2C_{12}H_8)$) ^3J(P–N–P)=65.4 Hz. $N_3P_3(O_2C_{12}H_8)[N(Me)–N=CH–R]_4$ (**7b**): 18.5 (d, 2P, *P*(N(Me)–N=CH–R), 26.0 (t, 1P, $P(O_2C_{12}H_8)$) ^3J(P–N–P)=70.9 Hz.
	$N_3P_3Cl_4(O_2C_{12}H_8)$ 13.3 (dd, 1P, $P(O_2C_{12}H_8)$), 25.2 (d, 2P, PCl_2), ^3J(P–N–P)=71 Hz.		$N_3P_3(O_2C_{12}H_8)[N(Me)–N=CH–R]_4$ (**7c**): 19.7 (d, 2P, *P*(N(Me)–N=CH–R), 26.6 (t, 1P, $P(O_2C_{12}H_8)$) ^3J(P–N–P)=70.9 Hz. $N_3P_3(O_2C_{12}H_8)[N(Me)–N=CH–R]_4$ (**7d**): 20.2 (d, 2P, *P*(N(Me)–N=CH–R), 26.7 (t, 1P, $P(O_2C_{12}H_8)$) ^3J(P–N–P)=65.4 Hz.
8	$N_3P_3Cl_6$ 19.5 (s)	$N_3P_3[N(Me)–NH_2]_6$ 29.5 (s, 3P, N_3P_3 ring)	$P_3N_3[N(Me)–N=CH–R]_6$ (**8b**): 17.31 (s) $P_3N_3[N(Me)–N=CH–R]_6$ (**8c**): 18.92 (s)

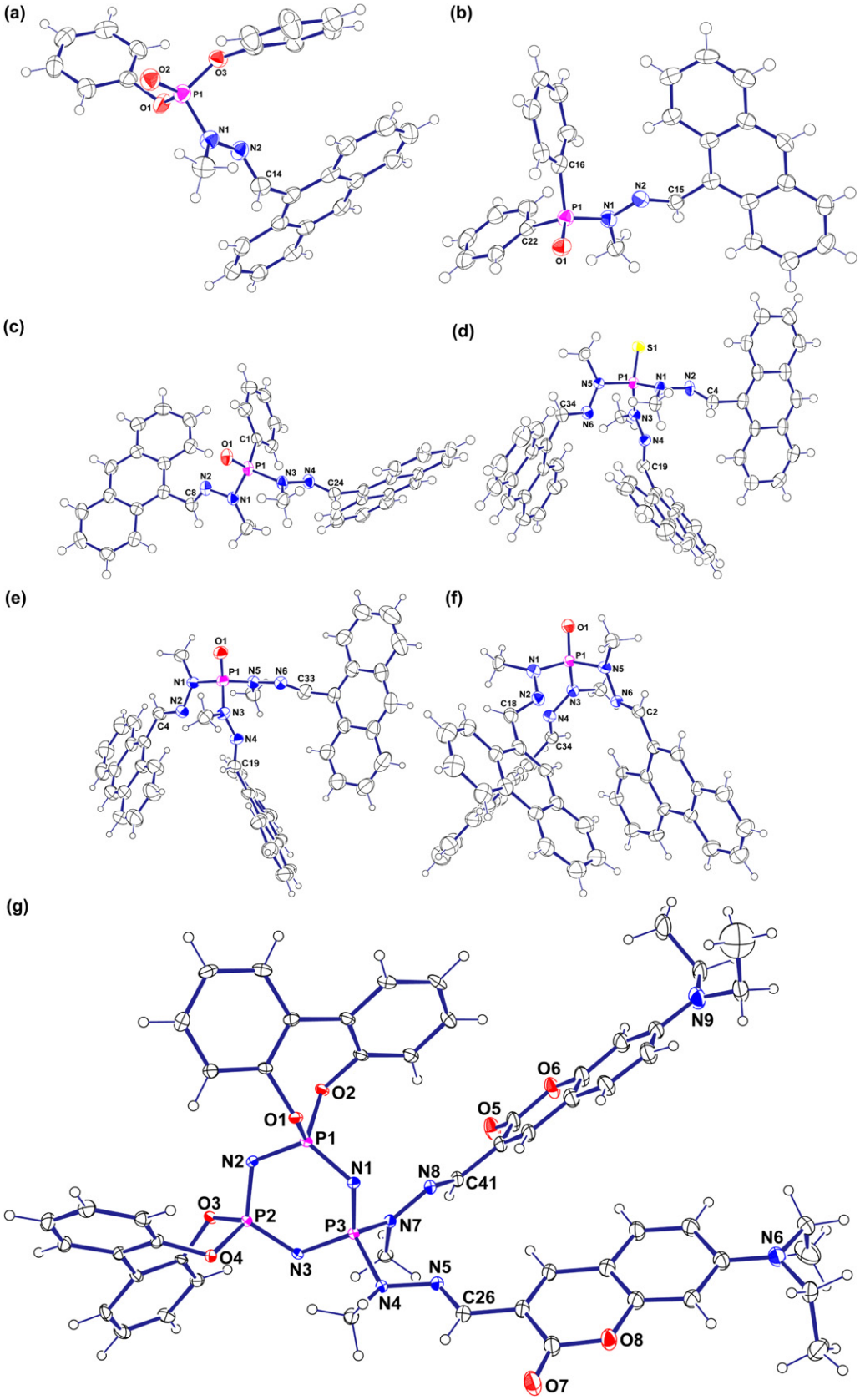


Fig. 1. Molecular structures of **1b** (a), **2b** (b), **3b** (c), **4b** (d), **5b** (e), **5c** (f) and **6d** (g) are shown with 50% ellipsoidal probability level (ORTEP diagrams).

Table 2
Selected bond parameters for the crystal structures of **1b**, **2b**, **3b**, **4b**, **5b**, **5c** and **6d**

Structure	Bond length (Å)		Bond angle (°)	
1b	P1–O2 1.452 (2)	P1–O1 1.578 (2)	O2–P1–O1 115.86 (12)	O2–P1–O3 115.99 (11)
	P1–O3 1.584 (2)	P1–N1 1.651 (2)	O1–P1–O3 100.15 (11)	O2–P1–N1 113.04 (13)
			O1–P1–N1 103.79 (11)	O3–P1–N1 106.48 (11)
2b	C16–P1 1.798 (3)	C22–P1 1.805 (3)	O1–P1–N1 117.77 (11)	O1–P1–C16 113.06 (11)
	N1–P1 1.676 (2)	O1–P1 1.477 (2)	N1–P1–C16 104.37 (11)	O1–P1–C22 111.63 (11)
			N1–P1–C22 103.30 (11)	C16–P1–C22 105.53 (11)
3b	C1–P1 1.788 (3)	N1–P1 1.685 (2)	O1–P1–N3 110.28 (10)	O1–P1–N1 113.08 (11)
	N3–P1 1.670 (2)	O1–P1 1.474 (2)	N3–P1–N1 104.63 (10)	O1–P1–C1 113.49 (11)
			N3–P1–C1 109.54 (11)	N1–P1–C1 105.34 (11)
4b	N1–P1 1.673 (2)	N3–P1 1.673 (3)	N1–P1–N3 104.83 (13)	N1–P1–N5 103.99 (13)
	N5–P1 1.677 (3)	P1–S1 1.926 (1)	N3–P1–N5 106.37 (13)	N1–P1–S1 115.05 (10)
			N3–P1–S1 113.42 (10)	N5–P1–S1 112.29 (10)
5b	P1–O1 1.443 (3)	P1–N3 1.653 (4)	O1–P1–N3 112.1 (2)	O1–P1–N1 110.35 (19)
	P1–N1 1.655 (4)	P1–N5 1.659 (4)	N3–P1–N1 108.29 (19)	O1–P1–N5 114.7 (2)
			N3–P1–N5 106.35 (19)	
5c	P1–O1 1.455 (5)	P1–N3 1.667 (5)	O1–P1–N3 113.3 (3)	O1–P1–N1 112.5 (3)
	P1–N1 1.678 (6)	P1–N5 1.684 (5)	N3–P1–N1 107.3 (3)	O1–P1–N5 111.8 (2)
			N3–P1–N5 105.4 (2)	
6d	N1–P1 1.576 (4)	N1–P3 1.590 (4)	N1–P1–N2 117.5 (2)	O1–P1–N2 111.0 (2)
	N2–P2 1.574 (4)	N2–P1 1.587 (4)	N1–P1–O2 113.2 (2)	O1–P1–O2 102.6 (2)
	N3–P2 1.567 (4)	N3–P3 1.601 (4)	N2–P1–O2 105.3 (2)	N3–P2–N2 118.7 (2)
	N4–P3 1.681 (4)	N7–P3 1.662 (4)	N3–P2–O3 113.1 (2)	N2–P2–O3 103.3 (2)
	O1–P1 1.583 (3)	O2–P1 1.593 (3)	N3–P2–O4 105.2 (2)	N2–P2–O4 113.4 (2)
	O3–P2 1.588 (4)	O4–P2 1.597 (3)	O3–P2–O4 102.20 (18)	N1–P3–N3 116.5 (2)
			N1–P3–N7 110.0 (2)	N3–P3–N7 108.2 (2)
			N1–P3–N4 111.0 (2)	N3–P3–N4 104.5 (2)
			N7–P3–N4 106.0 (2)	

instance also four different types of bond distances are observed (Table 2). A long distance of 1.601 (4) Å (P3–N3) and a short distance of 1.576 (4) Å (P1–N1) are observed. In addition, two other types of P–N distances are also observed within the P_3N_3 ring as follows, 1.574 (4) and 1.590 (4) Å for P2–N2 and P3–N1; 1.587 (4) and 1.567 (4) Å for P1–N2 and P2–N3, respectively.[13] Within the P_3N_3 ring the bond angle at P3 is the smallest (116.5 (2)°), while those observed at P2 (118.6 (2)°) and P1 (117.5 (2)°) are wider than the ideal values. Also the bond angles at nitrogen atoms are much wider than the ideal values. These trends are in keeping with sp^3 hybridization at phosphorus and an approximate sp^2 hybridization at nitrogen. The cyclophosphazene ring in **6d** is non planar; P1, P3, N1 are in one plane while N2, P2, N3 are in the other plane and showing the dihedral angle of 37.8° between them (Fig. 2). Two types of exocyclic P–N distances found at P3 are P3–N4 1.681 (4) Å and P3–N7 1.662 (4) Å.

The crystal packing of all these compounds showed strong intra- and intermolecular hydrogen bonding interactions (CH···O, C–H···π and π···π) that leads to the formation of various supramoleculer architectures. These aspects are not discussed here.

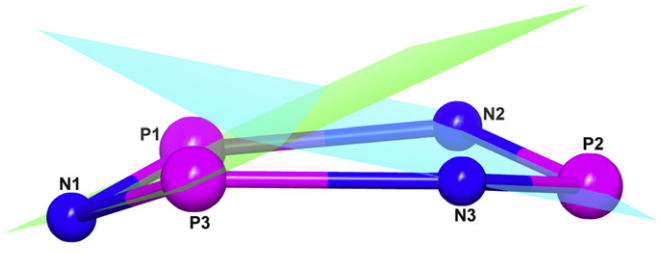


Fig. 2. Cyclophosphazene ring plane of compounds **6d**.

2.2. Absorption and emission spectra

The spectroscopic data of all the ligands are given in the Table 3. The absorption spectra of all the compounds in HEPES buffer (9:1 v/v of H_2O/DMSO, 10 mM, pH=7.4) are characterized by peaks both at high and low energies. In general, it has been found that on changing the number of chromophoric groups, absorption maxima also changes arbitrarily [cf. λ_{max} (ε): 265 (1.96×10^4), 375 (2.3×10^3) for **1a**; 266 (7.2×10^4), 371 (1.1×10^4) for **5a**; 262 (4.9×10^4), 375 (1.0×10^4) for **6a**; 295 (1.24×10^4), 371 (1.4×10^4) for **7a**] (Fig. 3). The observed spectra are typical for fluorophore-containing compounds and the absorptions are due to aromatic $\pi-\pi^*$ transitions.[8,9,14] The fluorescence spectra of all the four type of probes viz. pyrene (λ_{ext}=363 nm), anthracene (λ_{ext}=255 nm), phenanthrene (λ_{ext}=255 nm) and coumarin (λ_{ext}=413 nm) showed broad as well sharp peaks in the HEPES buffer (9:1 v/v of H_2O/DMSO, 10 mM, pH=7.4) solution (Fig. 4; Table 3). The pyrene series showed a broad band at 465 nm (**5a** and **7a**), 470 nm (**6a**) and 505 nm (**1a**). Interestingly, **5a** and **7a** showed higher intensity when compared to other compounds but **1a** showed emission band at longer wavelength. The anthracene series showed a broad

Table 3
Spectroscopic data of **1**–**8**

Compounds	λ_{max}/nm ($\varepsilon\times10^{-4}$)	λ_{em}/nm	ϕ_F
1a	265 (2.0), 377 (0.27)	505	0.009
1b	257 (2.6), 272 (2.4), 394 (0.28)	388, 408, 422	0.001
2b	245 (1.4), 278 (1.6), 396 (0.28)	394, 448	0.003
2c	257 (2.1), 320 (1.5)	338	0.002
2d	294 (0.47), 444 (1.8)	516	0.049
3b	260 (2.2), 402 (0.6)	360, 396, 421	0.002
3c	258 (1.7), 319 (0.11)	374	0.003
4b	263 (0.8), 378 (0.16)	428, 451	0.001
4c	256 (3.5), 327 (0.19)	376	0.002
5a	266 (7.0), 372 (1.05)	467	0.010
5b	247 (1.1), 283 (1.2), 361 (0.5)	393, 424	0.001
5c	258 (1.1), 339 (0.71)	375, 421	0.001
6a	261 (4.9), 367 (7.1)	471	0.011
6b	256 (3.8), 389 (0.15)	362, 392, 419	0.002
6c	251 (1.0), 329 (0.38)	369, 414	0.001
7a	290 (1.2), 372 (1.35), 396 (1.1)	468	0.016
7b	266 (2.5), 366 (0.5)	357, 426	0.001
7c	255 (2.5), 327 (1.2)	370	0.002
7d	274 (4.6), 423 (7.7)	530	0.022
8b	255 (4.0), 402 (0.8)	361, 390, 413	0.001
8c	253 (3.2), 325 (1.1)	370	0.003

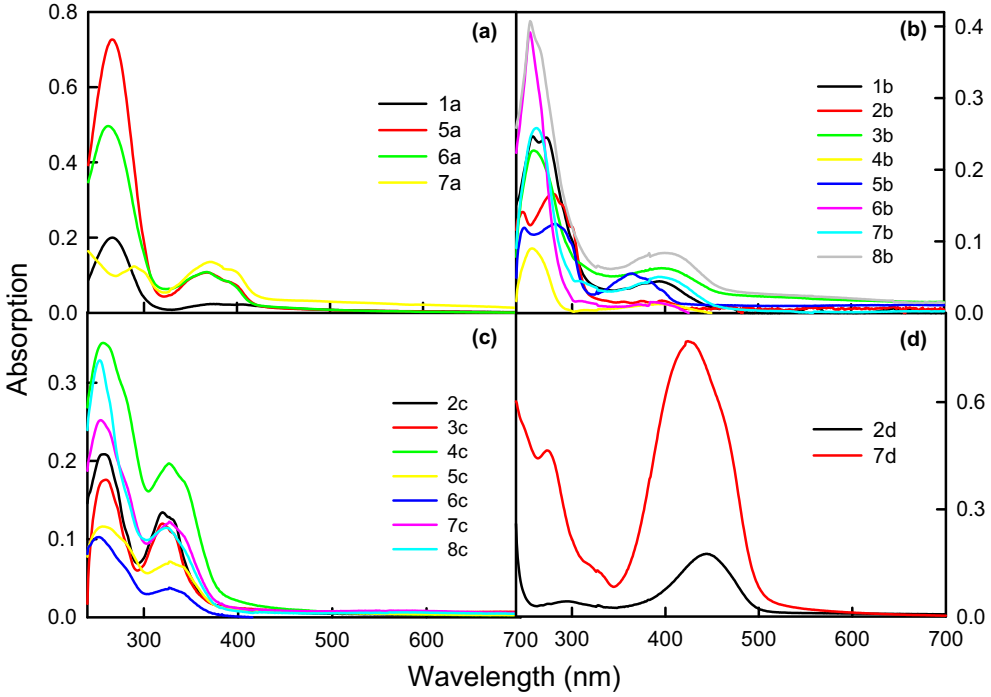


Fig. 3. UV–vis spectra of pyrene series (a), anthracene series (b), phenanthrene series (c) and coumarin series (d). Concentration of the HEPES buffer solution: 10.0 μM; 9:1 mixture of H_2O/DMSO; pH=7.4.

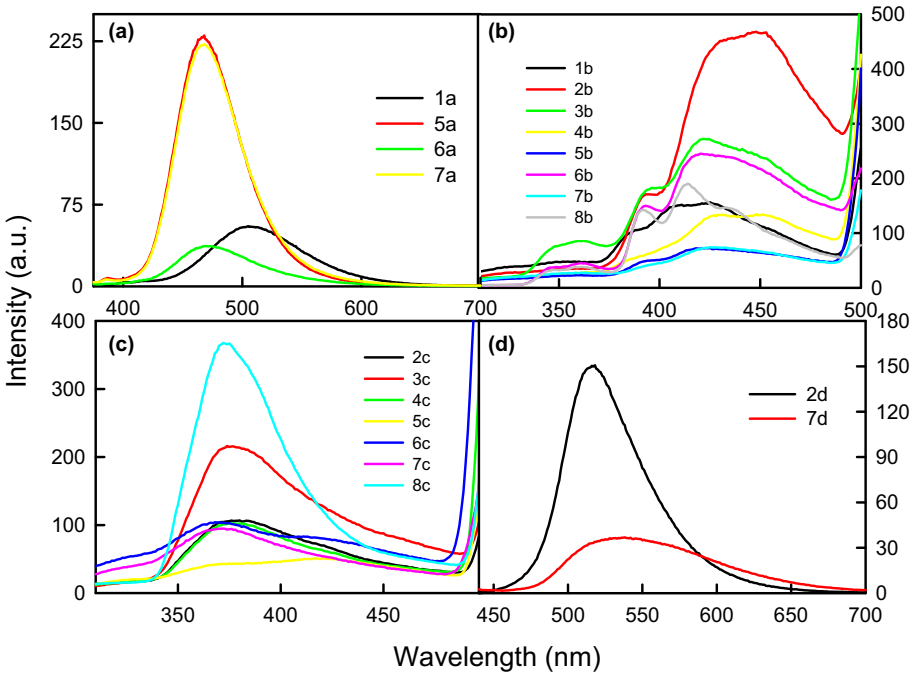


Fig. 4. (a) Fluorescence spectra of pyrene series (λ_{ext}=363 nm); (b) Fluorescence spectra of anthracene series (λ_{ext}=255 nm); (c) Fluorescence spectra of phenanthrene series (λ_{ext}=255 nm) and (d) Fluorescence spectra of coumarin series (λ_{ext}=413 nm). Concentration of the HEPES buffer solution: 10.0 μM; 9:1 mixture of H_2O/DMSO; pH=7.4.

band at ~420 nm along with some higher energy shoulders; **6b** showed a slightly higher intensity and more red-shifted emission bands. The phenanthrene series showed a broad band emission at ~370 nm with higher intensity for **3c** and **8c**, while **5c** showed a comparatively lower intensity. The coumarin series showed a broad band emission at ~515 nm with **2d** showing a higher intensity than **7d**.

3. Conclusion

We have shown a new synthetic strategy to build multi-chromophore containing molecular assemblies. Our methodology consists of utilizing phosphorus hydrazides as the functional precursors that could be elaborated by a condensation reaction strategy to the corresponding hydrazones. The type of aldehyde used

governs the property of the assembly. The number and orientation of such aldehydes allow a modulation of the property. Accordingly, in this study, we have shown the possibility to obtain photoactive assemblies using phosphorus atoms as the structural supports. Studies exploring the utility of such compounds in various applications including selective sensing of metal ions is underway.

4. Experimental section

4.1. Reagents

Solvents were received from S. D. Fine chemicals (India) and purified prior to use. $(PhO)_2P(O)Cl$, $Ph_2P(O)Cl$, $PhP(O)Cl_2$, pyrene-1-carboxaldehyde, anthracene-9-carboxaldehyde, phenanthrene-9-carboxaldehyde, 4-diethylaminosalicylaldehyde, diethylmalonate, 2,2′-dihydroxybiphenyl, hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) and pipyridine were purchased from Sigma–Aldrich, USA. (*S*)PCl_3 and (*O*)PCl_3 were purchased from Fluka (Switzerland). All the phosphorus hydrazones[15] and 7-(*N*,*N*′-diethylamino)-coumarin-3-aldehyde[16] were synthesized using reported procedures. *N*-Methylhydrazine (Me–NH–NH_2) was obtained as a gift from the Vikram Sarabhai Space Research Centre, Thiruvananthapuram, India and has been used as such.

4.2. Measurements

Melting points were measured using a JSGW melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a Bruker Vector-22 FTIR spectrophotometer operating from 400 to 4000 cm^{-1}. ^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectra were obtained on a JEOL-JNM LAMBDA 400 or JEOL-DELTA2 500 model spectrometer operating at 400 or 500 MHz (for ^1H), 100 or 125 MHz (for ^{13}C) and 202.5 MHz (for ^{31}P) in $CDCl_3$ solutions at room temperature. The chemical shifts are referenced with respect to TMS (for ^1H and ^{13}C) or 85% H_3PO_4 (for ^{31}P). Electrospray ionization–high resolution mass spectra (ESI–HRMS) were recorded on a MICROMASS QUATTRO II triple quadruple mass spectrometer. The ESI capillary was set at 3.5 kV and the cone voltage was 40 V. Steady state absorption and emission spectra were recorded on a Perkin–Elmer–Lambda 20 spectrophotometer and Varian Cary Eclipsed fluorimeter using a 10 mm quartz cell at room temperature. All the fluorescence measurements were taken on variable slit width ranging from 5:5 for pyrene series compounds, 10:10 for anthracene and phenanthrene series compounds and 5:2.5 for coumarin series compounds. In each case, the fluorescence quantum yield was determined by comparing the emission intensity of the sample with that of anthracene (ϕ=0.27) (for pyrenyl, anthracenyl and phenanthryl derivatives) and fluorescein (ϕ=0.85) in 0.1 N NaOH (for coumarinyl derivatives) using the equation:[17] $\phi_U=\phi_R(F_uA_R/F_RA_U)(n_U/n_R)^2$, where ϕ_U and ϕ_R are the fluorescence quantum yield of the sample and reference; F_U and F_R are the area under the fluorescence spectra of the sample and reference; A_U and A_R are the absorbance of the sample and reference (at the excitation wavelength); n_U and n_R are the refractive indices of the solvent used for the sample and reference.

4.3. Crystallography

Crystals suitable for X-ray diffraction were grown in a 1:1 mixture of $CHCl_3$/MeOH solution, except **6d**, which was grown from a 1:1 mixture of $CH_2Cl_2/CHCl_3$ solution. The single crystal X-ray data for **1b**, **2b**, **3b**, **4b**, **5b**, **5c** and **6d** were collected on a Bruker SMART APEX CCD diffractometer (Mo Kα, λ=0.71073 Å, 100 K). Complete hemispheres of data were collected using ω-scans (0.3°, up to 30 s/frame). Integrated intensities were obtained with SAINT+.[18a] Absorption corrections, where necessary, were made using SADABS.[18b] Structure solution and refinement was performed with the SHELXTL-package.[18c] The structures were solved by direct methods and completed by iterative cycles of DF syntheses and full-matrix least-squares refinement against F^2.[18c] Non-hydrogen atoms were refined with anisotropic displacement parameters. Details of the data collection and refinement parameters are given in Table 4.

Table 4
Crystallographic data and structure refinement details for **1b**–**6b**

	1b	2b	3b	4b	5b	5c	6d
Empirical formula	$C_{28}H_{23}N_2O_3P$	$C_{28}H_{23}N_2OP$	$C_{38}H_3N_4OP$	$C_{48}H_{39}N_6PS$	$C_{49}H_{40}C_{l3}$ N_6OP	$C_{48}H_{39}N_6OP$	$C_{111}H_{108}C_{l8}N_{18}O_{16}P_6$
Formula weight	466.45	434.45	590.64	762.88	866.19	746.82	2419.57
Temperature (K)	100 (2)	100 (2)	100 (2)K	153 (2)	273 (2)	100 (2)	100 (2)
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_12_12_1$	$P21/n$	$P-1$	$P-1$	$P-1$	$C2/c$	$P-1$
a (Å)	5.951 (2)	8.409 (3)	10.847 (4)	10.845 (5)	11.122 (6)	32.718 (5)	11.010 (4)
b (Å)	16.063 (6)	14.562 (6)	11.951 (5)	16.632 (5)	13.445 (7)	15.104 (5)	12.759 (4)
c (Å)	23.803 (8)	17.447 (7)	13.148 (5)	21.434 (5)	14.471 (8)	18.160 (5)	20.531 (7)
α (°)	90	90	77.937 (7).	96.565 (5)	81.166 (10)	90.00	86.616
β (°)	90	94.918 (7)	67.022 (6)	90.574 (5)	82.114 (11)	96.33	76.804
γ (°)	90	90	69.184 (6)	91.907 (5)	82.625 (12)	90.00	82.921
V (Å^3)	2275.3 (13)	2128.4 (14)	1461.8 (9)	3838 (2)	2105.3 (19)	8919 (4)	2785.3 (17)
Z	4	4	2	4	2	8	1
D_{calcd} (mg/m^3)	1.362	1.356	1.342	1.320	1.366	1.112	1.443
Abs. coeff. (mm^{-1})	0.155	0.154	0.134	0.170	0.302	0.102	0.363
F(000)	976	912	620	1600	900	3136	1254
Cryst size (mm^3)	0.08×0.05×0.04	0.08×0.04×0.03	0.09×0.08×0.05	0.11×0.08×0.05	0.10×0.06×0.04	0.08×0.06×0.04	0.19×0.08×0.06
θ range (°)	2.13 to 26.5	2.34 to 28.38	2.14 to 26.5	2.12 to 26.5	2.21 to 25.0	1.91 to 25.50	1.96 to 26.0
Index ranges	$-7\le h\le 7$	$-11\le h\le 11$	$-13\le h\le 10$	$-13\le h\le 13$	$-13\le h\le 9$	$-39\le h\le 25$	$-13\le h\le 13$
	$-20\le k\le 18$	$-11\le k\le 19$	$-14\le k\le 14$	$-15\le k\le 20$	$-15\le k\le 15$	$-18\le k\le 18$	$-9\le k\le 15$
	$-23\le l\le 29$	$-23\le l\le 22$	$-16\le l\le 15$	$-24\le l\le 26$	$-16\le l\le 17$	$-20\le l\le 22$	$-25\le l\le 24$
Reflections collected/unique	13207/4702	13709/5282	8471/5883	22397/15530	10796/7258	20781/7530	15689/10714
	[R(int)=0.0741]	[R(int)=0.0525]	[R(int)=0.0292]	[R(int) =0.0429]	[R(int)=0.0658]	[R(int)=0.0958]	[R(int)=0.0463]
Data/restraints/parameters	4702/0/308	5282/0/290	5883/0/399	15530/0/1015		7530/336/509	10714/2/727
Goodness-of-fit on F^2	1.094	1.098	1.065	0.996	0.976	0.958	1.053
Final R indices [$I>2\sigma(I)$]	R_1=0.0530	R_1=0.0604	R_1=0.0627	R_1=0.0679	R_1=0.0899	R_1=0.1203	R_1=0.0923
	wR_2=0.1182	wR_2=0.1458	wR_2=0.1610	wR_2=0.1670	wR_2=0.2255	wR_2=0.2909	wR_2=0.2478
R indices (all data)	R_1=0.0682	R_1=0.0976	R_1=0.0830	R_1=0.1045	R_1=0.1702	R_1=0.1958	R_1=0.1317
	wR_2=0.1321	wR_2=0.1926	wR_2=0.1932	wR_2=0.2080	wR_2=0.2925	wR_2=0.3435	wR_2=0.2973
Largest diff peak and hole (e Å^{-3})	0.367 and −0.584	0.551 and −0.655	0.530 and −0.539	0.643 and −0.551	0.404 and −0.538	0.427 and −0.324	2.055 and −0.634

4.4. General procedure for the synthesis of compounds 1a–8c

The phosphorus hydrazones **1a**–**8c** were synthesized by the following literature methods.[8,9,15] Quantitative amount of phosphorus hydrazide in MeOH (15 mL) was added dropwise to the solution of corresponding fluorophore-containing carboxaldehyde in hot MeOH (30 mL). The reaction mixture was stirred at 50 °C for 6 h. The yellow precipitate obtained was filtered, washed with hot methanol (2×5 mL) and recrystallized from a 1:1 mixture of CH_2Cl_2/*n*-hexane at 0 °C. The specific details of each reaction are given below.

Compound **1a**: Pyrene-1-carboxaldehyde (0.69 g, 3.00 mmol); {$(PhO)_2P(O)[N(Me)NH_2]$} (0.834 g, 3.00 mmol). Yield: 1.06 g, (72%). Mp: 118–120 °C. FT-IR (ν/cm^{-1}): 3667 (b), 3448 (m), 3040 (m), 2924 (m), 1614 (s), 1591 (s), 1489 (s), 1384 (s), 1287 (s), 1217 (s), 1191 (s), 1072 (s), 1026 (s), 987 (s), 950 (s). ^{1}H NMR (400 MHz, δ/ppm): 3.50 (d, 3H, −NC*H*$_3$, $^3J(^1H-^{31}P)$=8.04 Hz), 7.17–8.62 (m, 19H, pyrenyl/phenyl *H*) and 8.64 (s, 1H, C*H*=N). ^{13}C NMR (100 MHz, δ/ppm): 150.60, 138.11, 131.94, 131.37, 130.62, 128.65, 128.09, 127.42, 125.78, 125.41, 125.29, 124.74, 122.47, 120.74, 32.50. $^{31}P\{^1H\}$ NMR (202.5 MHz, δ/ppm): −5.00 (s). Anal. Calcd for $C_{30}H_{23}N_2O_3P$ from ESI–HRMS (*m*/*z*): [**1a**+H]$^+$=calculated 491.1525, found 491.1523; [2(**1a**)+H]$^+$=calculated 981.2971, found 981.2972.

Compound **1b**: Anthracene-9-carboxaldehyde (0.618 g, 3.00 mmol); {$(PhO)_2P(O)[N(Me)NH_2]$} (0.834 g, 3.00 mmol). Yield: 0.97 g (70%). Mp: 120 °C. FT-IR (ν/cm^{-1}): 3450 (b), 3041 (m), 1590 (s), 1488 (s), 1286 (s), 1191 (s), 988 (s), 950 (s). ^{1}H NMR (500 MHz, δ/ppm): 3.49 (d, 3H, −NC*H*$_3$, $^3J(^1H-^{31}P)$=8.0 Hz), 7.16–8.49 (m, 19H, anthracenyl/phenyl *H*), 8.6 (s, 1H, C*H*=N). ^{13}C NMR (125 MHz, δ/ppm): 150.60, 138.54, 131.49, 130.11, 128.98, 126.60, 125.37, 125.12, 120.71, 120.74, 32.62. $^{31}P\{^1H\}$ NMR (202.5 MHz, δ/ppm): −5.06 (s). Anal. Calcd for $C_{28}H_{23}N_2O_3P$ from ESI–HRMS (*m*/*z*): [M+H]$^+$=calculated 467.1525, found 467.1521; [2(**1b**)+H]$^+$=calculated 933.2971, found 933.3032.

Compound **2b**: Anthracene-9-carboxaldehyde (0.618 g, 3.00 mmol); {$Ph_2P(O)[N(Me)NH_2]$} (0.738 g, 3.00 mmol). Yield: 1.01 g, (78%). Mp: 150 °C. FT-IR (ν/cm^{-1}): 3422 (b), 3072 (m), 1590 (s), 1662 (s), 1591 (s), 1246 (s), 1205 (s), 1157 (s), 1123 (s), 1102 (s), 987 (s), 966 (s), 749 (s). ^{1}H NMR (400 MHz, δ/ppm): 3.51 (d, 3H, −NC*H*$_3$, $^3J(^1H-^{31}P)$=12.0 Hz), 7.15–8.80 (m, 19H, anthracenyl/phenyl *H*), 8.83 (s, 1H, C*H*=N). ^{13}C NMR (125 MHz, δ/ppm): 162.74, 131.83, 131.02, 129.75, 128.40, 127.36, 127.03, 125.74, 123.14, 122.71, 34.62. $^{31}P\{^1H\}$ NMR (202.5 MHz, δ/ppm): 32.76 (s). Anal. Calcd for $C_{28}H_{23}N_2O_3P$ from ESI–HRMS (*m*/*z*): [**2b**+H]$^+$=calculated 435.1626, found 435.1620.

Compound **2c**: Phenanthrene-9-carboxaldehyde (0.618 g, 3.00 mmol); {$Ph_2P(O)[N(Me)NH_2]$} (0.738 g, 3.00 mmol). Yield: 0.93 g (72%). Mp: 131–135 °C. FT-IR (ν/cm^{-1}): 3426 (b), 3053 (m), 2928 (m), 1686 (s), 1620 (m), 1527 (s), 1252 (s), 1155 (s), 961 (s), 727 (s), 595 (s). ^{1}H NMR (400 MHz, δ/ppm): 3.61 (d, 3H, −NC*H*$_3$, $^3J(^1H-^{31}P)$=10 Hz), 7.18–9.07 (m, 19H, phenanthrenyl/phenyl *H*), 9.46 (s, 1H, −C*H*=N). ^{13}C NMR (125 MHz, δ/ppm): 131.82, 131.69, 131.00, 129.75, 128.40, 127.35, 124.03, 125.72, 123.13, 122.70, 33.61. $^{31}P\{^1H\}$ NMR (202.5 MHz, δ/ppm): 30.82 (s). Anal. Calcd for $C_{28}H_{23}N_2O_3P$ from ESI–HRMS (*m*/*z*): [**2c**+H]$^+$=calculated 435.1626, found 435.1626.

Compound **2d**: 7-diethylamino-coumarin-3-aldehyde (0.736 g, 4.23 mmol); {$Ph_2P(O)[N(Me)–NH_2]$} (1.042 g, 4.23 mmol). Yield: 1.5 g (72%). Mp: 205 °C. FT-IR (ν/cm^{-1}): 3422 (b), 3056 (m), 2967 (m), 2928 (m), 1971 (s), 1700 (s), 1620 (s), 1518 (s), 1469 (s), 1377 (s), 1226 (s), 1134 (s), 955 (s), 906 (s), 799 (s). ^{1}H NMR (500 MHz, δ/ppm): 1.15 (t, 6H, −C*H*$_3$), 3.22 (s, 3H, −NC*H*$_3$, $^3J(^1H-^{31}P)$=9.0 Hz), 3.42 (q, 4H, −C*H*$_2$), 6.5 (s, 1H, aromatic *H*), 6.6 (d, 1H, aromatic *H*), 7.1–7.6 (m, 10H, aromatic *H*), 7.82 (s, 1H, −C*H*=N). ^{13}C NMR (125 MHz, δ/ppm): 136.79, 132.39, 132.31, 131.99, 128.33, 128.22, 44.88, 31.01, 12.44. $^{31}P\{^1H\}$ NMR (202.5 MHz, δ/ppm): 32.38 (s). Anal. Calcd for $C_{27}H_{28}N_3O_3P$ from ESI–HRMS (*m*/*z*): [**2d**+H]$^+$=calculated 474.1907, found 474.1942; [**2d**+Na]$^+$=calculated 496.1766, found 496.1739; [**2d**+CH_3OH+CH_3CN+H]$^+$=calculated 547.2474, found 547.2834; [2(**2d**)+Na]$^+$=calculated 969.3436, found 969.3644.

Compound **3b**: Anthracene-9-carboxaldehyde (0.412 g, 2.00 mmol); {$Ph_2P(O)[N(Me)NH_2]_2$} (0.214 g, 1.00 mmol). Yield: 0.448 g (76%). Mp: 208–210 °C. FT-IR (ν/cm^{-1}): 3424 (b), 3046 (m), 2926 (m), 1674 (s), 1621 (s), 1583 (s), 1515 (s), 1463 (s), 1439 (s), 1331 (s), 1245 (s), 1209 (s), 1156 (s), 979 (s), 735 (s). ^{1}H NMR (400 MHz, δ/ppm): 3.42 (d, 3H, −NC*H*$_3$), $^3J(^1H-^{31}P)$=7.6 Hz, 7.05–8.29 (m, 22H, anthracenyl/phenyl *H*), 8.55 (s, 1H, −C*H*=N). ^{13}C NMR (100 MHz, δ/ppm): 135.82, 133.55, 132.17, 131.31, 129.79, 128.64, 128.32, 126.81, 126.04, 125.13, 125.03, 31.24. $^{31}P\{^1H\}$ NMR (202.5 MHz, δ/ppm): 25.54 (s). Anal. Calcd for $C_{38}H_{31}N_4OP$ from ESI–HRMS (*m*/*z*): [**3b**+H]$^+$=calculated 591.2314, found 591.2313; [**3b**+CH_3OH+CH_3CN+H]$^+$=calculated 664.2836, found 664.3214.

Compound **3c**: Phenanthrene-9-carboxaldehyde (0.412 g, 2.00 mmol); {$Ph_2P(O)[N(Me)NH_2]_2$} (0.214 g, 1.00 mmol). Yield: 0.436 g (74%). Mp: 135 °C. FT-IR (ν/cm^{-1}): 3446 (b), 2925 (m), 2855 (s), 1744 (s), 1690 (s), 1623 (s), 1525 (s), 1494 (s), 1447 (s), 1246 (s), 1203 (s), 1153 (s), 1109 (s), 1074 (s), 956 (s). ^{1}H NMR (500 MHz, δ/ppm): 3.43 (d, 3H, −NC*H*$_3$, $^3J(^1H-^{31}P)$=11.85 Hz), 7.24–8.70 (m, 22H, phenanthrenyl/phenyl *H*), 9.51 (s, 1H, −C*H*=N). ^{13}C NMR (125 MHz, δ/ppm): 137.31, 137.19, 133.22, 133.16, 130.66, 12930, 128.87, 128.23, 127.14, 126.64, 125.41, 122.84, 122.38, 30.57. $^{31}P\{^1H\}$ NMR (202.5 MHz, δ/ppm): 27.19 (s). Anal. Calcd for $C_{38}H_{31}N_4OP$ from ESI–HRMS (*m*/*z*): [**3c**+H]$^+$=calculated 591.2314, found 591.2312; [**3c**+CH_3OH+CH_3CN+H]$^+$=calculated 664.2836, found 664.3217; [2(**3c**)+H]$^+$=calculated 1181.4549, found 1181.4579.

Compound **4b**: Anthracene-9-carboxaldehyde (0.618 g, 3.00 mmol); {$P(S)[N(Me)NH_2]_3$} (0.214 g, 1.00 mmol). Yield: 0.594 g (78%). Mp: 250–252 °C. FT-IR (ν/cm^{-1}): 3435 (b), 3047 (m), 2926 (m), 1675 (s), 1662 (s), 1462 (s), 1257 (s), 1228 (s), 1147 (s), 954 (s), 731 (s), 597 (s). ^{1}H NMR (400 MHz, δ/ppm)=3.53 (d, 9H, −NC*H*$_3$, $^3J(^1H-^{31}P)$=12.44 Hz), 6.71–8.26 (m, 27H, anthracenyl *H*), 8.33 (s, 2H, −C*H*=N). ^{13}C NMR (100 MHz, δ/ppm): 135.89, 135.74, 131.16, 129.66, 128.28, 127.76, 127.41, 125.67, 125.15, 124.83, 32.78. $^{31}P\{^1H\}$ NMR (202.5 MHz, δ/ppm): 74.64 (s). Anal. Calcd for $C_{48}H_{39}N_6SP$ from ESI–HRMS (*m*/*z*): [**4b**+H]$^+$=calculated 763.2773, found 763.2770; [**4b**+CH_3OH+H]$^+$=calculated 795.3035, found 795.2681.

Compound **4c**: Phenanthrene-9-carboxaldehyde (0.618 g, 3.00 mmol); {$P(S)[N(Me)NH_2]_3$} (0.214 g, 1.00 mmol). Yield: 0.534 g (70%). Mp: 120 °C. FT-IR (ν/cm^{-1}): 3440 (b), 2924 (m), 1568 (m), 1493 (s), 1449 (s), 1246 (s), 1148 (s), 953 (s), 825 (s), 747 (s). ^{1}H NMR (500 MHz, δ/ppm): 3.58 (d, 9H, −NC*H*$_3$, $^3J(^1H-^{31}P)$=9.1 Hz), 7.00–8.80 (m, 27H, phenanthrenyl *H*), 8.82 (s, 2H, −C*H*=N). ^{13}C NMR (125 MHz, δ/ppm): 136.89, 136.77, 131.18, 130.67, 130.34, 129.65, 128.82, 128.07, 126.9, 126.84, 126.45, 125.14, 122.89, 122.22, 32.34. $^{31}P\{^1H\}$ NMR (202.5 MHz, δ/ppm): 75.20 (s). Anal. Calcd for $C_{48}H_{39}N_6SP$ from ESI–HRMS (*m*/*z*): [**4c**+H]$^+$=calculated 763.2773, found 763.2775.

Compound **5a**: Pyrene-1-carboxaldehyde (0.690 g, 3.00 mmol); {$P(O)[N(Me)NH_2]_3$} (0.182 g, 1.00 mmol). Yield: 0.605 g (74%). Mp: 130 °C (d). FT-IR (ν/cm^{-1}): 3437 (b), 3037 (m), 2925 (m), 1677 (s), 1626 (s), 1595 (s), 1463 (s), 1412 (s), 1381 (s), 1268 (s), 1178 (s), 1148 (s), 1058 (s), 961 (s). ^{1}H NMR (400 MHz, δ/ppm): 3.51 (d, 3H, −NC*H*$_3$, $^3J(^1H-^{31}P)$=9.2 Hz), 7.25–9.44 (m, 27H, pyrenyl *H*), 9.92 (s, 1H, −C*H*=N). ^{13}C NMR (100 MHz, δ/ppm): 130.57, 128.55, 128.00, 127.85, 127.35, 125.82, 125.33, 125.03, 124.87, 44.38. $^{31}P\{^1H\}$ NMR (202.5 MHz, δ/ppm): 16.36 (s). Anal. Calcd for $C_{54}H_{39}N_6OP$ from ESI–HRMS (*m*/*z*): [**5a**+H]$^+$=calculated 819.3001, found 819.3001.

Compound **5b**: Anthracene-9-carboxaldehyde (0.618 g, 3.00 mmol); {$P(O)[N(Me)NH_2]_3$} (0.182 g, 1.00 mmol). Yield: 0.60 g (80%). Mp: 220–222 °C. FT-IR (ν/cm^{-1}): 3419 (b), 3048 (m), 2924 (m), 1622 (s), 1516 (s), 1463 (s), 1443 (s), 1308 (s), 1019 (s), 1494 (s),

1447 (s), 966 (s), 732 (s), 601 (s). ^{1}H NMR (500 MHz, δ/ppm): 3.57 (d, 9H, −NCH_3, $^3J(^1H-^{31}P)$=7.5 Hz), 6.70–8.26 (m, 27H, anthracenyl H), 8.41 (s, 3H, −C*H*=N). ^{13}C NMR (125 MHz, δ/ppm): 135.96, 135.83, 131.2, 129.76, 128.34, 127.83, 127.45, 125.73, 125.11, 124.9, 32.43. ^{31}P{^{1}H} NMR (202.5 MHz, δ/ppm): 16.45 (s). Anal. Calcd for $C_{48}H_{39}N_6OP$ from ESI–HRMS (*m*/*z*): [**5b**+H]$^+$=calculated 747.3001, found 747.3003; [**5b**+CH_3OH+CH_3CN+H]$^+$=calculated 820.3523, found 820.3882.

Compound **5c**: Phenanthrene-9-carboxaldehyde (0.618 g, 3.00 mmol); {P(O)[N(Me)NH_2]$_3$} (0.182 g, 1.00 mmol). Yield: 0.537 g (72%). Mp: 138–140 °C. FT-IR (ν/cm^{-1}): 3444 (b), 2927 (m), 1618 (m), 1447 (s), 1253 (s), 1150 (s), 965.57 (s), 746 (s), 722s. ^{1}H NMR (500 MHz, δ/ppm): 3.51 (d, 9H, −NCH_3, $^3J(^1H-^{31}P)$=10.0 Hz), 6.99–8.79 (m, 27H, phenanthrenyl *H*), 8.80 (s, 3H, −C*H*=N). ^{13}C NMR (125 MHz δ/ppm): 137.015, 136.89, 131.158, 130.653, 130.357, 129.508, 128.859, 128.154, 126.947, 126.475, 125.035, 122.89, 122.211, 31.988. ^{31}P{^{1}H} NMR (202.5 MHz, δ/ppm): 16.8 (s). Anal. Calcd for $C_{48}H_{39}N_6OP$ from ESI–HRMS (*m*/*z*): [**5c**+H]$^+$=calculated 747.3001, found 747.3004; [**5c**+CH_3OH+CH_3CN+H]$^+$=calculated 820.3523, found 820.3919.

Compound **6a**: Pyrene-1-carboxaldehyde (0.460 g, 2.00 mmol); {$N_3P_3(O_2C_{12}H_8)_2$[N(Me)NH_2]$_2$} (0.593 g, 1.00 mmol). Yield: 0.712 g (70%). Mp: 240 °C (d). FT-IR (ν/cm^{-1}): 3446 (b), 3038 (m), 2925 (m), 1600 (s), 1501 (s), 1475 (s), 1438 (s), 1382 (s), 1263 (s), 1229 (s), 1093 (s), 967 (s). ^{1}H NMR (400 MHz, δ/ppm): 3.63 (d, 3H, −NCH_3, $^3J(^1H-^{31}P)$=4.8 Hz), 7.25–8.70 (m, 34H, pyrenyl/phenyl *H*), 8.73 (s, 1H, −C*H*=N). ^{13}C NMR (100 MHz, δ/ppm): 129.58, 129.08, 127.5, 125.87, 125.29, 124.98, 123.04, 122.12. 34.11. ^{31}P{^{1}H} NMR (202.5 MHz, δ/ppm): 19.8 (t, 1P, *P*(N(Me)–N=CH–R)), 26.6 (d, 2P, *P*($O_2C_{12}H_8$), ^3J(P–N–P)=70.9 Hz). Anal. Calcd for $C_{60}H_{42}N_7O_4P_3$ from ESI–HRMS (*m*/*z*): [**6a**+H]$^+$=calculated 1018.2589, found 1018.2587; [**6a**+Na]$^+$=calculated 1040.2409, found 1040.2274.

Compound **6b**: Anthracene-9-carboxaldehyde (0.412 g, 2.00 mmol); {$N_3P_3(O_2C_{12}H_8)_2$[N(Me)NH_2]$_2$} (0.593 g, 1.00 mmol). Yield: 0.66 g (69%). Mp: 182–184 °C. FT-IR (ν/cm^{-1}): 3446 (b), 2924 (m), 1672 (s), 1439 (s), 1283 (s), 1171 (s), 1092 (s), 964 (s), 878 (s), 732 (s). ^{1}H NMR (500 MHz, δ/ppm): 3.63 (d, 6H, −NCH_3, $^3J(^1H-^{31}P)$=9.0 Hz), 7.12–8.97 (m, 34H, anthracenyl/phenyl *H*), 8.98 (s, 2H, −C*H*=N). ^{13}C NMR (125 MHz, δ/ppm): 148.56, 135.35, 134.21, 132.23, 130.05, 129.38, 128.24, 127.30, 125.93, 125.75, 123.63, 122.12, 32.72. ^{31}P{^{1}H} NMR (202.5 MHz, δ/ppm): 19.0 (t, 1P, *P*(N(Me)–N=CH–R)), 26.4 (d, 2P, *P*($O_2C_{12}H_8$), ^3J(P–N–P)=70.9 Hz). Anal. Calcd for $C_{56}H_{42}N_7O_4P_3$ from ESI–HRMS: *m*/*z*: [**6b**+H]$^+$=calculated 970.2589, found 970.2585.

Compound **6c**: Phenanthrene-9-carboxaldehyde (0.412 g, 2.00 mmol); {$N_3P_3(O_2C_{12}H_8)_2$[N(Me)NH_2]$_2$} (0.593 g, 1.00 mmol). Yield: 0.581 g (60%). Mp: 175–178 °C. FT-IR (ν/cm^{-1}): 3447 (b), 2926 (m), 1618 (m), 1475 (s), 1438 (s), 1264 (s), 1228 (s), 1171 (s), 1093 (s), 967 (s), 916 (s), 782 (s). ^{1}H NMR (500 MHz, δ/ppm): 3.48 (d, 6H, −NCH_3, $^3J(^1H-^{31}P)$=9.5 Hz), 7.17–8.70 (m, 34H, phenanthrenyl/phenyl *H*), 8.72 (s, 2H, −C*H*=N). ^{13}C NMR (125 MHz, δ/ppm): 148.44, 137.04, 136.91, 131.95, 130.62, 129.83, 129.67, 127.75, 126.90, 126.39, 125.84, 125.36, 122.88, 122.4, 122.07, 32.23. ^{31}P{^{1}H} NMR (202.5 MHz, δ/ppm): 19.8 (t, 1P, *P*(N(Me)–N=CH–R)), 26.6 (d, 2P, *P*($O_2C_{12}H_8$), ^3J(P–N–P)=70.9 Hz). Anal. Calcd for $C_{56}H_{42}N_7O_4P_3$ from ESI–HRMS (*m*/*z*): [**6c**+H]$^+$=calculated 970.2589, found 970.2587; [**5b**+CH_3OH+CH_3CN+H]$^+$=calculated 1043.3117, found 1043.3539.

Compound **7a**: Pyrene-1-carboxaldehyde (0.92 g, 4.00 mmol); {$N_3P_3(O_2C_{12}H_8)$[N(Me)–NH_2]$_4$} (0.701 g, 1.00 mmol). Yield: 0.916 g (68%). Mp: 158–160 °C. FT-IR (ν/cm^{-1}): 3449 (b), 3037 (m), 2924 (m), 1675 (s), 1596 (s), 1463 (s), 1438 (s), 1380 (s), 1222 (s), 1176 (s), 1094 (s), 961 (s). ^{1}H NMR (400 MHz, δ/ppm): 3.57 (d, 3H, −NCH_3, $^3J(^1H-^{31}P)$=8.56 Hz), 7.24–8.77 (m, 42H, pyrenyl/phenyl *H*), 9.42 (s, 2H, −C*H*=N). ^{13}C NMR (100 MHz, δ/ppm): 135.76, 131.33, 130.66, 129.42, 127.85, 127.43, 125.77, 125.21, 124.95, 122.98, 32.54. ^{31}P{^{1}H} NMR (202.5 MHz, δ/ppm)=19.9 (d, 2P, *P*(N(Me)–N=CH–R)), 26.8 (t, 1P, *P*($O_2C_{12}H_8$), ^3J(P–N–P)=65.4 Hz). Anal. Calcd for $C_{60}H_{42}N_7O_4P_3$ from ESI–HRMS (*m*/*z*): [**7a**+H]$^+$=calculated 1348.4223, found 1348.4226.

Compound **7b**: Anthracene-9-carboxaldehyde (0.824 g, 4.00 mmol); {$N_3P_3(O_2C_{12}H_8)$[N(Me)–NH_2]$_4$} (0.701 g, 1.00 mmol). Yield: 0.813 g (65%). Mp: 220 °C. FT-IR (ν/cm^{-1}): 3425 (b), 3048 (m), 1621 (s), 1440 (s), 1222 (s), 1176 (s), 1177 (s), 963 (s), 881 (s), 732 (s). ^{1}H NMR (500 MHz, δ/ppm): 3.63 (d, 12H, −NCH_3, $^3J(^1H-^{31}P)$=10.0 Hz), 7.09–8.55 (m, 44H, anthracenyl/phenyl *H*), 9.59 (s, 4H, −C*H*=N). ^{13}C NMR (125 MHz, δ/ppm): 148.96, 135.61, 131.48, 130.02, 129.65, 129.33, 128.58, 128.05, 126.04, 125.82, 125.10, 32.74. ^{31}P{^{1}H} NMR (202.5 MHz, δ/ppm): 18.5 (d, 2P, *P*(N(Me)–N=CH–R)), 26.0 (t, 1P, *P*($O_2C_{12}H_8$), ^3J(P–N–P)=70.9 Hz). Anal. Calcd for $C_{76}H_{60}N_{11}O_2P_3$ from ESI–HRMS (*m*/*z*): [**7b**+H]$^+$=calculated 1252.4223, found 1252.4221.

Compound **7c**: Phenanthrene-9-carboxaldehyde (0.824 g, 4.00 mmol); {$N_3P_3(O_2C_{12}H_8)$[N(Me)–NH_2]$_4$} (0.701 g, 1.00 mmol). Yield: 0.876 g (70%). Mp: 165–168 °C. FT-IR (ν/cm^{-1}): 3448 (b), 3060 (m), 2927 (m), 1685 (s), 1614 (s), 1496 (s), 1442 (s), 1222 (s), 1176 (s), 1094 (s), 1042 (s), 964 (s), 748 (s). ^{1}H NMR (500 MHz, δ/ppm): 3.53 (d, 12H, −NCH_3, $^3J(^1H-^{31}P)$=8.8 Hz), 7.20–8.83 (m, 44H, phenanthrenyl/phenyl *H*), 8.84 (s, 4H, −C*H*=N). ^{13}C NMR (125 MHz, δ/ppm): 148.75, 136.57, 131.36, 130.58, 130.33, 129.72, 129.62, 127.60, 126.88, 126.8, 126.57, 125.42, 122.81, 122.36, 32.22. ^{31}P{^{1}H} NMR (202.5 MHz, δ/ppm): 19.7 (d, 2P, *P*(N(Me)–N=CH–R)), 26.6 (t, 1P, *P*($O_2C_{12}H_8$), ^3J(P–N–P)=70.9 Hz). Anal. Calcd for $C_{76}H_{60}N_{11}O_2P_3$ from ESI–HRMS (*m*/*z*): [**7c**+H]$^+$=calculated 1252.4223, found 1252.4221.

Compound **7d**: 7-diethylamino-coumarin-3-aldehyde (0.500 g, 2.874 mmol); {$N_3P_3(O_2C_{12}H_8)$[N(Me)–NH_2]$_4$} (0.359 g, 0.71 mmol). Yield: 0.630 g (63%). Mp: 182–186 °C. FT-IR (ν/cm^{-1}): 3423 (b), 2971 (m), 2928 (m), 1712 (s), 1608 (s), 1518 (s), 1468 (s), 1354 (s), 1258 (s), 1132 (m), 964 (s), 907 (s), 741 (s). ^{1}H NMR (400 MHz, δ/ppm): 1.14 (t, 24H, −CH_3), 3.33 (q, 8H (broad), −CH_2), 3.25 (s, 12H, −NCH_3, $^3J(^1H-^{31}P)$=8.0 Hz), 6.40 (s, 4H, aromatic *H*), 6.45 (m, 4H, aromatic *H*) 7.1–7.47 (m, 16H, aromatic *H*), 7.72 (s, 2H, −C*H*), 8.1 (s, 2H, −C*H*=N). ^{13}C NMR (125 MHz, δ/ppm): 162.47, 156.21, 150.57, 137.06, 129.86, 115.42, 109.31, 97.08, 44.83, 32.27, 12.45. ^{31}P{^{1}H} NMR (202.5 MHz, δ/ppm): 20.2 (d, 2P, *P*(N(Me)–N=CH–R)), 26.7 (t, 1P, *P*($O_2C_{12}H_8$), ^3J(P–N–P)=65.4 Hz). Anal. Calcd for $C_{72}H_{80}N_{15}O_{10}P_3$ from ESI–HRMS (*m*/*z*): [**7d**+H]$^+$=calculated 1408.5504, found 1408.5507; [**7d**+Na]$^+$=calculated 1430.5323, found 1430.5186.

Compound **8b**: Anthracene-9-carboxaldehyde (1.236 g, 6.00 mmol); {N_3P_3[N(Me)NH_2]$_6$} (0.701 g, 1.00 mmol). Yield: 0.920 g (60%). M.pt.: 132–134 °C. FT-IR (ν/cm^{-1}): 3430 (b), 2924 (m), 1668 (s), 1443 (s), 1207 (s), 1149 (s), 965 (s), 882 (s), 731 (s), 598 (s). ^{1}H NMR (500 MHz, δ/ppm): 3.67 (d, 18H, −NCH_3, $^3J(^1H-^{31}P)$=6.5 Hz), 7.06–8.94 (m, 54H, anthracenyl *H*), 8.96 (s, 6H, −C*H*=N). ^{13}C NMR (125 MHz, δ/ppm): 135.33, 132.21, 131.49, 130.01, 129.36, 129.20, 128.55, 128.33, 127.76, 126.04, 125.85, 125.12, 123.60, 32.93. ^{31}P{^{1}H} NMR (202.5 MHz, δ/ppm): 17.3068 (s). Anal. Calcd for $C_{96}H_{78}N_{15}P_3$ from ESI–HRMS (*m*/*z*): [**8b**+H]$^+$=calculated 1535.5856, found 1535.5934.

Compound **8c**: Phenanthrene-9-carboxaldehyde (1.236 g, 6.00 mmol); {N_3P_3[N(Me)NH_2]$_6$} (0.701 g, 1.00 mmol). Yield: 0.981 g (64%). Mp: 152–155 °C. FT-IR (ν/cm^{-1}): 3448 (b), 3055 (m), 2925 (m), 1566 (m), 1493 (s) 1448 (s), 1248 (s), 1203 (s), 1152 (s), 967 (s), 747 (s). ^{1}H NMR (500 MHz, δ/ppm): 3.61 (d, 18H, −NCH_3, $^3J(^1H-^{31}P)$=30.0 Hz), 7.23–8.81 (m, 54H, phenanthrenyl *H*), 8.83 (s, 6H, −C*H*=N). ^{13}C NMR (125 MHz, δ/ppm): 141.30, 136.08, 131.43, 130.60, 130.18, 129.79, 129.01, 127.26, 126.83, 126.34, 125.93, 125.34, 122.84, 122.72, 32.43. ^{31}P{^{1}H} NMR (202.5 MHz, δ/ppm): 18.92 (s).

Anal. Calcd for $C_{96}H_{78}N_{15}P_3$; ESI–HRMS (m/z): $[M+H]^+$=calculated 1535.5856, found 1535.5935.

Acknowledgements

We thank the Department of Science and Technology (DST), India for financial support. V.C. and M.D.P. are thankful to the Department of Science and Technology for a J.C. Bose National fellowship and DST-SERC Fast Track Scheme for Young Scientists Fellowship, respectively. B.M. thankful to CSIR, New Delhi, India for a Senior Research Fellowship. This work is also supported by the Bioinorganic Chemistry Initiative, DST, India.

Supplementary data

Scanned images of $^{31}P\{^1H\}$ NMR and ESI–HRMS spectra. CCDC 809367 (**1b**), 809368 (**2b**), 809369 (**3b**), 809370 (**4b**), 809371 (**5b**), 809372 (**5c**) and 806357 (**6d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223/336 033; e-mail: deposit@ccdc.cam.ac.uk]. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2011.06.073.

References and notes

1. (a) Schneider, R.; Köllner, C.; Weber, I.; Togni, A. *Chem. Commun.* **1999**, 2415; (b) Chandrasekhar, V.; Nagendran, S. *Chem. Soc. Rev.* **2001**, *30*, 193; (c) Koprowski, M.; Sebastián, R. M.; Maraval, V.; Zablocka, M.; Cadierno, V.; Donnadieu, B.; Igau, A.; Caminade, A. M.; Majoral, J. P. *Organometallics* **2002**, *21*, 4680; (d) Darcos, V.; Duréault, A.; Taton, D.; Gnanou, Y.; Marchand, P.; Caminade, A.; Majoral, J. P.; Destarac, M.; Leising, F. *Chem. Commun.* **2004**, 2110.
2. (a) Kim, C.; Jeong, Y.; Jung, I. *J. Organomet. Chem.* **1998**, *9*, 570; (b) Casado, C. M.; Cuadrado, I.; Morán, M.; Alonso; Barranco, M.; Losada, J. *Appl. Organomet. Chem.* **1999**, *13*, 245; (c) Murfee, H. J.; Thoms, T. P. S.; Greaves, J.; Hong, B. *Inorg. Chem.* **2000**, *39*, 5209; (d) Ropartz, L.; Morris, R. E.; Cole-Hamilton, D. J.; Foster, D. F. *Chem. Commun.* **2001**, 361; (e) Ropartz, L.; Foster, D. F.; Morris, R. E.; Slawin, A. M. Z.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **2002**, 1997.
3. (a) Kotz, J. C.; Painter, W. J. *J. Organomet. Chem.* **1971**, *32*, 231; (b) Gates, D. P.; McWilliams, A. R.; Ziembinski, R.; Liable-Sands, L. M.; Guzei, I. A.; Yap, G. P. A.; Rheingold, A. L.; Manners, I. *Chem.—Eur. J.* **1998**, *4*, 1497; (c) Bats, J. W.; Ma, K.; Wagner, M. *Acta Crystallogr.* **2002**, *C58*, m129; (d) Lerner, H. W.; Scholz, S.; Bats, J. W.; Bolte, M.; Wagner, M. *J. Organomet. Chem.* **2002**, *664*, 94.
4. (a) Stasch, A.; Ferbinteanu, M.; Prust, J.; Zheng, W.; Cimpoesu, F.; Magull, J.; Schmidt, H. G.; Noltemeyer, M. *J. Am. Chem. Soc.* **2002**, *124*, 5441; (b) Kumar, S. S.; Reddy, N. D.; Roesky, H. W.; Vidovic, D.; Magull, J.; Winter, R. F. *Organometallics* **2003**, *22*, 3348; (c) Kumar, S. S.; Roesky, H. W. *Dalton Trans.* **2004**, 3927; (d) Kumar, S. S.; Roesky, H. W.; Andronesi, O.; Baldus, M.; Winter, R. F. *Inorg. Chim. Acta* **2005**, *358*, 2349.
5. Chandrasekhar, V.; Andavan, G. T. S.; Nagendran, S.; Krishnan, V.; Azhakar, R.; Butcher, R. J. *Organometallics* **2003**, *22*, 976.
6. (a) Majoral, J. P.; Badri, M.; Caminade, A. M.; Delmas, M.; Gaset, A. *Inorg. Chem.* **1988**, *27*, 3873; (b) Mitjaville, J.; Caminade, A. M.; Majoral, J. P. *Chem. Commun.* **1994**, 2161; (c) Caminade, A. M.; Majoral, J. P. *Chem. Rev.* **1994**, *94*, 1183; (d) Mitjaville, J.; Caminade, A. M.; Daran, J. C.; Donnadieu, B.; Majoral, J. P. *J. Am. Chem. Soc.* **1995**, *117*, 1712; (e) Galliot, C.; Caminade, A. M.; Dahan, F.; Majoral, J. P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1477; (f) Brauge, L.; Magro, G.; Caminade, A. M.; Majoral, J. P. *J. Am. Chem. Soc.* **2001**, *123*, 6698; (g) Slany, M.; Caminade, A. M.; Majoral, J. P. *Tetrahedron Lett.* **1996**, *37*, 9053; (h) Mongin, O.; Krishna, T. R.; Werts, M. H. V.; Caminade, A. M.; Majoral, J. P.; Blanchard-Desce, M. *Chem. Commun.* **2006**, 915.
7. (a) Katti, K. V.; Reddy, V. S.; Singh, P. R. *Chem. Soc. Rev.* **1995**, *24*, 97; (b) Wang, M.; Volkert, E. W.; Singh, P. R.; Katti, K. K.; Lusiak, P.; Katti, K. V.; Barnes, C. L. *Inorg. Chem.* **1994**, *33*, 1184; (c) Singh, P. R.; Jimenez, H.; Katti, K. V.; Volkert, W. A.; Barnes, C. L. *Inorg. Chem.* **1994**, *33*, 736; (d) Reddy, V. S.; Katti, K. V.; Barnes, C. L. *Organometallics* **1994**, *13*, 2391.
8. (a) Chandrasekhar, V.; Pandian, B. M. *Acc. Chem. Res.* **2009**, *42*, 1047; (b) Chandrasekhar, V.; Azhakar, R.; Andavan, G. T. S.; Krishnan, V.; Zacchini, S.; Bickley, J. F.; Steiner, A.; Butcher, R. J.; Kögerler, P. *Inorg. Chem.* **2003**, *42*, 5989; (c) Chandrasekhar, V.; Andavan, G. T. S.; Azhakar, R.; Pandian, B. M. *Inorg. Chem.* **2008**, *47*, 1922; (d) Chandrasekhar, V.; Azhakar, R.; Pandian, B. M.; Bickley, J. F.; Steiner, A. *Eur. J. Inorg. Chem.* **2008**, *7*, 1116; (e) Chandrasekhar, V.; Pandian, B.; Azhakar, R.; Boomishankar, R.; Steiner, A.; Vittal, J. J.; Houri, A.; Clećrac, R. *Inorg. Chem.* **2008**, *47*, 4918; (f) Chandrasekhar, V.; Pandian, B. M.; Vittal, J. J.; Clećrac, R. *Inorg. Chem.* **2009**, *48*, 1148; (g) Chandrasekhar, V.; Azhakar, R.; Murgesapandian, B.; Senapati, T.; Bag, P.; Pandey, M. D.; Maurya, S. K.; Goswami, D. *Inorg. Chem.* **2010**, *49*, 4008; (h) Chandrasekhar, V.; Pandey, M. D.; Gopal, K.; Azhakar, R. *Dalton Trans.* doi:10.1039/c1dt10294j
9. (a) Chandrasekhar, V.; Pandey, M. D.; Bag, P.; Pandey, S. *Tetrahedron* **2009**, *65*, 4540; (b) Chandrasekhar, V.; Bag, P.; Pandey, M. D. *Tetrahedron* **2009**, *65*, 9876; (c) Chandrasekhar, V.; Pandey, M. D.; Das, B.; Mahanti, B.; Senapati, T. *Indian J. Chem., Sect. A* **2011**, *50A*, 453.
10. Vilkov, L. V.; Sadova, N. I.; Zilberg, I. Y. *Zh. Strukt. Khim.* **1967**, *8*, 528.
11. Wingerter, S.; Pfeiffer, M.; Murso, A.; Lustig, C.; Stey, T.; Chandrasekhar, V.; Stalke, D. *J. Am. Chem. Soc.* **2001**, *123*, 1381.
12. Chandrasekhar, V.; Justin Thomas, K. R. *Struct. Bonding* **1993**, *81*, 41.
13. Mani, N. V.; Ahmad, F. R.; Barnes, W. H. *Acta Crystallogr.* **1965**, *19*, 693.
14. (a) Behera, K.; Pandey, M. D.; Porel, M.; Pandey, S. *J. Chem. Phys.* **2007**, *127*, 184501; (b) Chandrasekhar, V.; Kumar, A.; Pandey, M. D. *J. Organomet. Chem.* **2010**, *695*, 74; (c) Pandey, M. D.; Mishra, A. K.; Chandrasekhar, V.; Verma, S. *Inorg. Chem.* **2010**, *49*, 2020.
15. (a) Carriedo, G. A.; Fernndez-Catuxo, L.; Alonso, F. J. G.; Gmez-Elipe, P.; Gonzlez, P. A. *Macromolecules* **1996**, *29*, 5320; (b) Majoral, J. P.; Kraemer, R.; Navech, J.; Mathias, F. *Tetrahedron* **1976**, *32*, 2633.
16. (a) Ray, D.; Bharadwaj, K. P. *Inorg. Chem.* **2008**, *47*, 2252; (b) Wu, J.-S.; Liu, W.-M.; Zhuang, X.-Q.; Wang, F.; Wang, P.-F.; Tao, S.-L.; Zhang, X.-H.; Wu, S.-K.; Lee, S.-T. *Org. Lett.* **2007**, *9*, 33.
17. (a) Dawson, W. R.; Windsor, M. W. *J. Phys. Chem.* **1968**, *72*, 3251; (b) Paeker, C. A.; Ress, W. T. *Analyst* **1960**, *85*, 587.
18. (a) *SMART and SAINT Software Reference Manuals (Ver. 6.45)*; Bruker Analytical X-ray Systems: Madison, WI, 2003; (b) Sheldrick, G. M. *SADABS: a Software for Empirical Absorption Correction (Ver. 2.05)*; University of Gottingen: Gottingen, Germany, 2002; (c) Sheldrick, G. M. *SHELXTL (Ver. 6.12)*; Bruker AXS: Madison, WI, 2001.